Pestic. Sci. 1998, **53**, 104–106

Communication to the Editor

Simple and Sensitive Method for Determination of Tetramethylthiuram Disulphide (Thiram)

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(Received 2 December 1996; revised version received 10 October 1997; accepted 17 December 1997)

Abstract: A rapid, simple, direct and sensitive method has been developed for the determination of thiram (tetramethylthiuram disulphide) based on the formation of copper dimethyldithiocarbamate complex, which is rendered water-soluble by a cationic surfactant, cetytrimethylammonium bromide (CTAB). The method has been applied to the determination of thiram in synthetic mixtures, grain (wheat) samples and vegetables. © 1998 SCI

Pestic. Sci., **53**, 104–106 (1998)

Key words: thiram; copper; CTAB; spectrophotometry; analysis

1 INTRODUCTION

Thiram is a protective fungicide which is used on both foliage and fruit to control a variety of pests (of fruit, vegetables and ornamentals). Most of the methods used to determine thiram are based upon that of Clark *et al.*,[1] in which dithiocarbamates are decomposed in an acidic medium to yield carbon disulphide (CS_2) which is absorbed in methanolic potassium hydroxide yielding potassium methylxanthate which is then titrated iodimetrically.

Here we present a simple, sensitive and relatively rapid method in which thiram is converted into copper dimethyldithiocarbamate complex, and is solubilised in water by cetyltrimethylammonium bromide (CTAB).

2 EXPERIMENTAL

2.1 Equipment and reagents

All absorbances were measured on an SP-20 spectronic spectrophotometer. The pH measurements were carried out on an Elico pH meter. All solvents and reagents were of analytical reagent grade. Tetramethylthiuram disulphide (thiram) was recrystallised from ethanol to known purity. A 1 g litre^{-1} solution of thiram was prepared in boiling sodium hydroxide (0·1 M) which was standardised[2] titrimetrically using mercuric acetate as titrant and diphenylcarbazone as an indicator in acetate buffer and diluted with 0·1 M NaOH as desired. Copper sulfate solution (1 g litre^{-1}) was prepared in acidulated distilled water and standardised.[3] CTAB solution (10 g litre^{-1}) was prepared in distilled water. Acetate buffer was prepared by dissolving sodium acetate trihydrate (68 g; Glaxo) in water (400 ml) and adjusting the pH to 5·5 by adding glacial acetic acid (25–30 ml, Glaxo) and making the total volume to 500 ml. Stock solutions of other elements, cations and anions (whose interferences were to be studied) were prepared by mixing solutions of the elements to give the required composition.

2.2 Procedures

2.2.1 *Preparation of calibration curve*

A series of solutions containing 4·4–132·5 μg of thiram were used to prepare a calibration curve. To a known

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TABLE 1
Determination of Thiram in Synthetic Mixtures

No.	*Composition and percentage*	*Amount of thiram (μg)*		
		Calculated	*Found*	*Rel. error (%)*
1	Thiram (50) NaDDC[a] (20) Vapam (20) Nabam (10)	30·0	30·1	0·3
2	Thiram (60) Ziram (20) NaDDC (10) Nabam (10)	50·0	50·3	0·6

[a] Sodium diethyldithiocarbamate.

volume (⩽2 ml) of sample solution containing 4·4–132·5 μg of thiram, acetate buffer (pH 5·5; 2·0 ml) copper sulfate solution (1 g litre^{-1}; 1·0 ml) and CTAB solution (10 g litre^{-1}; 1·0 ml) were added and diluted to 10 ml with distilled water. The absorbance of a part of this solution was measured at 430 nm, against a reagent blank prepared under similar conditions.

2.2.2 Determination of thiram in synthetic mixtures
Mixtures of thiram with nabam (disodium ethylenebisdithiocarbamate), sodium dimethyldithiocarbamate, sodium diethydithiocarbamate and ziram in various proportions were prepared. Ziram and thiram were extracted into chloroform (10 ml) which were then evaporated to 2 ml on a hot water-bath, and the remainder evaporated by a gentle current of dry air. The residue was dissolved in sodium hydroxide solution (0·1 M); ziram is soluble in the cold and could be separated from thiram which dissolved on boiling. The sample is then treated as described above in Section 2.2.1. Results of the determination are given in Table 1.

2.2.3 Determination of thiram in grains and vegetables
The procedure was applied for the determination of thiram in grains (wheat) and cabbage. A known amount of thiram was sprayed on grains and cabbage and after 15–20 min the sprayed sample was crushed finely, homogenised in a mixer and shaken mechanically for 1 h. Chloroform (20 ml) was added to the mixture, which was then filtered. The residue in the funnel was washed with chloroform (3 × 10 ml). The extracts were evaporated down to 2 ml and the remaining solvent removed in a current of dry air at room temperature. The residue was dissolved in boiling sodium hydroxide solution (0·1 M) and thiram was determined by the general procedure. The results are given in Table 2.

TABLE 2
Determination of Thiram in Grain and Cabbage

Sample	*Amount of thiram (μg)[a]*	
	Calculated	*Found*
Grain (Wheat)	40·0	39·8
	80·0	79·7
Cabbage	35·0	34·7
	90·0	89·8

[a] $N = 3$; 20 g of grain or cabbage was used.

3 RESULTS AND DISCUSSION

3.1 Absorption spectra

The absorption spectra of copper dimethyldithiocarbamate complex were recorded in CTAB micellar medium and in 50% acetone solution against a reagent blank. The complex absorbs at 395 nm in acetone solution and at 430 nm in the presence of CTAB (Fig. 1).

3.2 Effect of pH

The absorbance was maximum when the pH of the solution was 3·5–8·0.

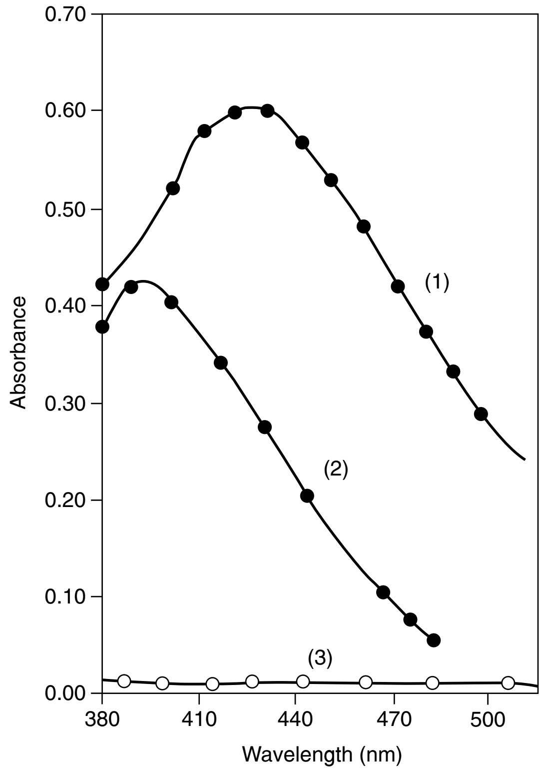

Fig. 1. Absorption spectra of (1) copper dimethyldithiocarbamate complex in CTAB; (2) copper dimethyldithiocarbamate complex in 50% acetone; (3) reference reagent blank. Thiram 88·3 μg; $CuSO_4 . 5\ H_2O$ (1 g litre^{-1}) 1·0 ml; CTAB (10 g litre^{-1}) 1·0 ml.

3.3 Effect of reagent and CTAB

One millilitre of 1 g $litre^{-1}$ copper sulphate solution and 1·0 ml of 10 g $litre^{-1}$ CTAB were sufficient to give maximum absorbance.

3.4 Effect of standing time

The absorbance of the complex remained practically constant for more than 24 h.

3.5 Composition of the complex

The composition of the complex was studied by Job's method of continuous variation and the mole ratio method was 1 : 1 (Cu : thiram). CTAB stabilises the complex by its micellar action.

3.6 Beer's law and sensitivity

A calibration graph for thiram at 430 nm was linear over the concentration range 0·44–13·25 mg $litre^{-1}$ of thiram under the optimum conditions tested above. Ten replicate determinations on sample solutions containing 88·3 μg of thiram gave a mean absorbance of 0·60 with a RSD of 0·86%. The molar absorptivity and Sandell's sensitivity (for an absorbance of 0·001) were $1{\cdot}63 \times 10^4$ M^{-1} cm^{-1} and 0·0147 $\mu g\ cm^{-2}$, respectively.

3.7 Interference

The following foreign ions (in mg) did not interfere in the determination of 88·3 μg of thiram: acetate (70), bromide (30), oxalate (25), tartrate (20), nitrate (35), chloride (30), sulphate (26), metabisulphite (0·01), Pb^{2+}(1·3), Zn^{2+}(1·0), Bi^{3+}(0·80), Cd^{2+}(0·82) and Mn^{2+}(0·2).

Interference by some dithiocarbamates like sodium monomethyldithiocarbamate, sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate, disodium ethylenebisdithiocarbamate was avoided by pre-extracting thiram into chloroform, the other dithiocarbamates remaining in the aqueous phase. Zinc ethylenebisdithiocarbamate and zinc dimethyldithiocarbamate could be separated from thiram by dissolving them in cold 0·1 M sodium hydroxide.

4 CONCLUSIONS

The sensitivity of the present method is much increased due to micellar action of the surfactant; a minimum 0·44 $\mu g\ ml^{-1}$ of thiram equivalent to 0·278 $\mu g\ ml^{-1}$ of evolved carbon disulphide can be determined which is superior to published methods.[4–6] Moreover, the present method does not involve an extraction step, thus making it easier to perform. The simplicity, sensitivity and wide applicability of this method make it the method of choice.

REFERENCES

1. Clark, D. G., Baum, H., Stanley, E. L. & Hester, W. E., *Anal. Chem.*, **23** (1951) 1842–6.
2. Rao, A. L. J., Malik, A. K. & Paul, Y., *J. Ind. Acad. Forensic Sci.*, **31** (1992) 19–24.
3. Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis*, 4th edn. Longman (ELBS London), 1978, p. 321.
4. Lowen, W. K., *J. Assoc. Off Agr. Chemists*, **36** (1953) 484–92.
5. Cullen, T. E., *Anal. Chem.*, **36** (1964) 221–4.
6. Chmiel, Z., *Chem. Anal.* (*Warsaw*), **24** (1978) 505–11.
7. Rangaswamy, J. R., Poornima, P. & Majumder, S. K., *J. Assoc. Off. Anal. Chemists*, **53** (1970) 519.